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New Chiral Liquid Crystal Compounds: (S)-(+)-4-[4-(Methyl)-1,3-dioxolan-2-yl]-phenyl-4-*n*-alkoxybenzoates and 4-*n*-alkoxycinnamates

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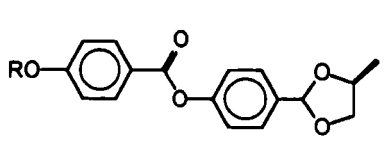
New liquid crystal compounds, (*S*)-(+)-[4-(methyl)-1,3-dioxolan-2-yl]phenyl-4-*n*-alkoxybenzoates, **I**, and (*S*)-(+)-[4-(methyl)-1,3-dioxolan-2-yl]phenyl-4-*n*-alkoxycinnamates, **II**, have been synthesized and the thermotropic liquid-crystalline behaviour investigated. The compounds did not exhibit a chiral smectic C phase. The mesophases present in these compounds are cholesteric and smectic A phases. The transition temperatures of series **II** are higher than those for series **I**.

Keywords: Liquid crystals, 1,3-dioxolane ring, smectic A and cholesteric phase.

INTRODUCTION

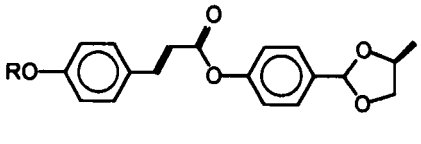
The possibility that chiral tilted smectic liquid crystals would exhibit ferroelectricity was predicted by Meyer and co-workers in 1975.[1] Subsequent interest in the field has increased tremendously with the development of the SSFLC technique developed by Clark and Lagerwall.[2] Moreover, considerable synthetic efforts are now being aimed at synthesis of new ferroelectic liquid crystal materials suitable for application in electronic devices. Liquid crystal displays using ferroelectic liquid crystals are important due to their shorter response time. Various optically active compounds with the 1,3-dioxane, 1,3-oxathiane or 1,3-dithiane ring have been synthesized and investigated.[3–7]

In this paper we wish to report the synthesis of (*S*)-(+)-4-[4-(methyl)-1, 3-dioxolan-2-yl]phenyl-4-*n*-alkoxybenzoates **I** and 4-*n*-alkoxycinnamates **II** and their mesomorphic behaviour.



SERIES I

$R = C_nH_{2n+1}$ (n = 8, 12, 16)



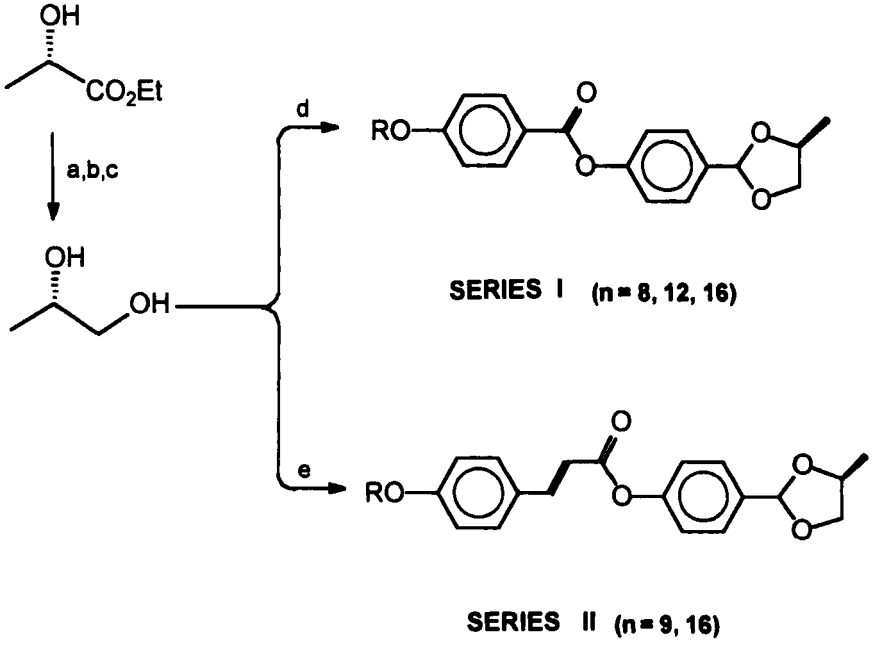
SERIES II

$R = C_nH_{2n+1}$ (n = 9, 16)

SYNTHESIS

The chiral starting material for the two series is (*S*)-ethyl lactate, readily available in high enantiomeric purity.[8] The synthesis is carried out as outlined in Scheme 1.

(*S*)-(−)Ethyl lactate was protected into its tetrahydropyranyl ether and then reduced to the corresponding ether of propylene glycol with lithium aluminium



a. DHP, HCl, MeOH, b. $LiAlH_4$, ether; c. PPTS, MeOH; d. $ROPhCO_2PhCHO$, H^+,

e. $ROPhCH{=}CHCO_2PhCHO$, H^+

SCHEME 1

hydride, using a procedure reported in the literature.[9] However, the preparation of the tetrahydropyranil ether yields two diastereomeric products since the hetero ring introduces a second asymmetric carbon, but this is not a problem in the development of the synthesis, because the removal of the tetrahydropyranyl protecting group catalyzed by PPTS destroys the second asymmetric carbon atom and gives the 1,2-propanediol which was converted to the acetals of series **I** and **II** under standard conditions.

RESULTS AND DISCUSSION

The acetalization reaction yielded two diastereomeric products which were characterized by ^{1}H NMR (300 MHz). In this final step it was necessary to isolate the *trans* isomer. Normally, about four recrystallizations were needed. In the case that the *cis* isomer could not be removed by recrystallization, column chromatography was used to obtain the *trans* isomer. For example, the ^{1}H NMR spectrum data for the unpurified $n = 9$ compound of series **II** showed C-2 proton signals for the 1,3-dioxolane ring of the *cis* and *trans* isomers at $\delta = 6{,}10$ and 6,24 ppm, respectively. Therefore, the removal of the *cis* isomer in both series can be checked by the disappearance of the *cis* isomer peak.

The liquid crystal phases and transition temperatures for series I and II are presented in Tables 1 and 2. None of the compounds exhibited the chiral smectic C (Sc*) phase, but only smectic A and cholesteric phases.

As can be seen from Tables 1 and 2, the transition temperatures of the compounds of series I without the cinnamic moiety are lower than those for the corresponding compounds of series II.

The reasons for the absence of a smectic C phase are probably related to the anisotropic form of the 1,3-dioxolane ring and the absence of a dipole moment perpendicular to the molecular axis. In heterocyclic systems, the mesomorphic behaviour depends fundamentally on the type of configurational isomerism adopted by the

TABLE 1

Transition temperatures (°C) for series I

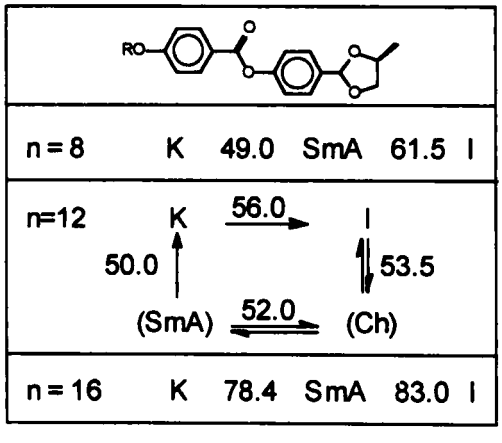
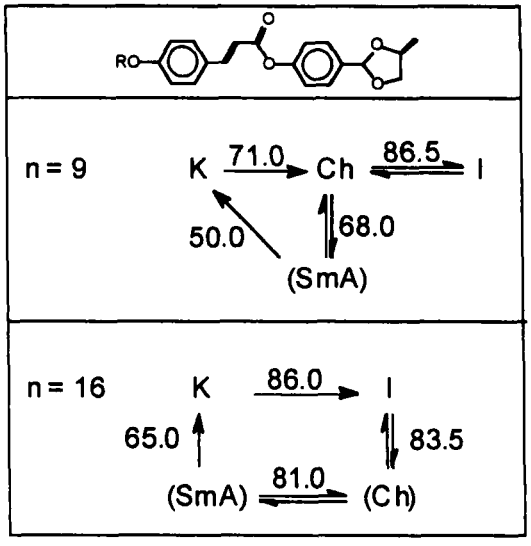


TABLE 2

Transition temperatures (°C) for series II



ring system. Thus, it is possible to predict for 1,4-disubstituted six-membered rings that the ring will adopt a well-defined conformation, usually the chair form. Since compounds with equatorial substituents are generally more stable, *trans*-1,4-isomers which can adopt the equatorial-equatorial positions are thermodynamically more stable than their *cis*-1,4-isomers. On the other hand, in the 1,3-dioxolane ring there is no corresponding minimum energy conformation of the ring and therefore also no conformational preference exists for a given substituents position.[10] The most stable conformation that 2,4-disubstituted-1,3-dioxolane ring will adopt is related to steric effects between substituents on C-2, C-4 and C-5 carbon atoms. Molecular models suggest that the conformation leading to the formation of the *trans* isomer is favored due to fewer steric interactions.[11] Moreover, in the *cis*-2,4-disubstituted-1,3-dioxolane ring there are unfavorable 1,3-pseudo-diaxiais interactions. The *trans* conformation for the 1,3-dioxolane ring holds the substituents in pseudo-axial and pseudo-equatorial positions while the *cis* conformation holds them in pseudo-axial or pseudo-equatorial.

Another fact that supports for the correct identification of the *cis* and *trans* isomers is based on the ^{1}H NMR spectra. The *cis* isomer shows an upfield chemical shift for the C-2 proton, while the *trans* isomer displays a downfield chemical shift.[10,11] For example, the ^{1}H NMR spectrum datas for the unpurified $n=9$ compound of series II showed C-2 proton signals for the 1,3-dioxolane ring of the *cis* and *trans* isomers at $\delta = 6{,}10$ and 6,24 ppm, respectively.

The existence of mesophases in these compounds is closely associated with the configuration (linearity) of the molecules. The *cis*-conformation causes larger deviations from linearity than the trans-conformation. The absence of mesophases with *cis* isomers are thus related to conformational factors.

EXPERIMENTAL

The transition temperatures for all compounds were determined by optical microscopy using a Leitz Ortholux polarizing microscope with a Mettler FP 52 heating stage. Purifications by column chromatography were carried out on silica gel (Merck 60cc). The IR spectra were recorded using KBr discs with a Perkin-Elmer model 283 spectrometer and the ^{1}H NMR spectra were recorded at 60 MHz (Varian T-60) and 300 MHz (Bruker HX-300). (*S*)-(−)-Ethyl lactate was purchased from Aldrich, and solvents and reagents were used as received from suppliers unless otherwise specified. Analytical thin-layer chromatography (TLC) was conducted on Merck aluminum plates with 0.2 mm of silica gel 60F-254.

Ethyl (S)-2-(Tetrahydro-2-pyranoxy)propanoate.[9] 3,4-Dihydro-2*H*-pyrano (0,12 mol, 10,5 g) and HCl 12 *N* (10 drops) were added to a solution of the (*S*)-(−)-ethyl lactate (0,12 mol, 15,0 g) and methanol (200 ml). The solution was stirred at room temperature for 8 h. Na_2CO_3(3 g) was added and stirring continued for 2 h. The material was filtered, concentrated on a rotary evaporator and distilled at reduced pressure to give 20,6 g (85%) of product with bp 74–76°C (0,7 mmHg). I.R. (film) υ_{max}: 2950, 2830, 1730, 1430, 1350, 1240, 1170, 1130–1070, 970, 890 and 610 cm^{-1}.

(S)-2-(Tetrahydro-2-pyranoxy)-1-propanol. Lithium aluminium hydride (0,08 mol, 2,90 g) was suspended in dry ether (100 ml). Ethyl (*S*)-2-(Tetrahydro-2-pyranoxy) propanoate (0,12 mol, 20,6 g) dissolved in dry ether (200 ml) was added dropwise at 0°C over 1 h. The solution was stirred for an additional 15 h at room temperature. Water (7,0 ml), sodium hydroxide (7,0 ml, 10%) and water (21 ml) were added slowly to give insoluble aluminates. The white granular precipitate was filtered off and washed with ether. The combined filtrate and washings were dried over magnesium sulfate and then concentrated and distilled at reduced pressure to give 13,9 g (72%) of product with bp 76–78°C (3 mmHg).

I.R. (film) υ_{max} : 3020, 2950, 2830, 1600, 1430, 1350, 1170, 970, 800 and 650 cm^{-1}.

(S)-(+)-1,2-Propanediol. A solution of (*S*)-2-(tetrahydro-2-pyranoxy)-1-propanol (0,087 mol, 13,9 g) and PPTS-Pyridinium *p*-Toluene sulfonate (0,0087 mol) in ethanol (50 ml) was stirred at 60°C for 4 h. The solvent was evaporated in vacuo, and the residue distilled to afford 5,30 g (80%) of (*S*)-(+)-1,2-Propanediol.

$[\alpha]_D^{25} = +15{,}5°$ (neat) I.R. (film) υ_{max}: 3350, 2930, 1450, 1380, 1300, 1140, 1050, 920 and 860 cm^{-1}; ^{1}H NMR (60 MHz, TMS, $CDCl_3$) $\delta = 1{,}2$ (*d*, 2H, $J = 6{,}0$ Hz, CH_3); 3,6–4,0 (*m*, 3H) and 5,1 (broad, 2H).

Representative Procedure for Preparing Acetals (Series I and II)

(S)-(+)-4'-[4-(Methyl)-1,3-dioxolane-2-yl]phenyl-4-n-nonyloxycinnamate. (*S*)-(+)-1,2-Propanediol (1,4 mmol), 4'-(4-*n*-noniloxycinnamoyloxy) benzaldehyde (1,4 mmol) and monohydrate *p*-toluene sulfonic acid (1%) were refluxed in a Dean-Stark apparatus for 12 h. The reaction vessel was cooled and $NaHCO_3$ (3 g) was added. The

mixture was stirred for 30 min, the solvent evaporated and the crystalline product recrystallized four times from ethanol to yield 0,8 mmol (57%) of the *trans* isomer. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) $\delta = 1{,}16$ (3H, *t*, $J = 7{,}50$Hz, CH_3); 1,52 (12H, *m*, CH_2); 1,61 (3H, *d*, $J = 6{,}00$ Hz, CH_3CH); 2,06 (2H, *m*, CH_2); 4,23 (2H, *t*, $J = 7{,}00$ Hz, CH_2O); 4,39 (1H, *dd*, $J = 7{,}55$Hz, CH_2CH); 4,52 (1H, *dd*, $J = 7{,}95$Hz, CH_2CH); 4,62 (1H, *m*, $CHCH_3$); 6,24 (1H, *s*, CH); 6,60 (1H, *d*, $J = 16{,}0$Hz, CH=CH); 6,80 (2H, *d*, $J = 8{,}00$Hz, Ar); 7,40 (2H, *d*, $J = 8{,}00$Hz, Ar); 7,70 (4H, *d*, $J = 8{,}00$ Hz, Ar) and 7,90 (1H, *d*, $J = 16{,}0$ Hz, CH=CH).

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